

CHAPTER III EXPERIMENTAL



3.1 Materials

3.1.1 Vegetable Oils

Vegetable oils used in this research were coconut oil and palm kernel oil. The crude CCO was obtained from Thai Taksin Company (Prachuap Kirikun province). While crude PKO was from Chumporn Palm Oil Industry Public Company Limited (Chumporn province).

3.1.2 Chemicals

All chemicals used in the experiment are shown in Table 3.1. They were used without further purification.

3.2 Equipment

3.2.1 Transesterification of Vegetable Oils Using Homogeneous Catalysts

A 500-ml three-necked flask equipped with a reflux condenser, thermometer and a sampling port was used in the experiment. The flask was immersed in a constant temperature-water bath and a magnetic stirrer was used to provide agitation. The experimental set-up is shown in Figure 3.1.

3.2.2 Transesterification of Vegetable Oils Using Heterogeneous Catalysts

The experimental set-ups used were different depending on the operating temperature. Studies at room temperature were done on the set-up described in 3.2.1.

Table 3.1 Chemicals used in the research

Name	Source	Purity
Methanol	Carlo Erba	99.9% (p.a.)
Sodium Hydroxide	Lab-Scan	99.0 % (AR)
Sodium Sulfate	Riedel-deHaen	99.0% (Anhydrous, AR)
Potassium Carbonate	Riedel-deHaen	98-100% (purified)
Sodium Carbonate	Riedel-deHaen	99.5-100% (Anhydrous, extra pure)
Calcium Carbonate	Riedel-deHaen	98.5-100% (extra pure, precipitated)
Acetonitrile	Carlo Erba	HPLC Grade
Acetone	Carlo Erba	HPLC Grade
Methyl Esters Mixture	Fluka	Standards for chromatography
Methyl Laurate	Fluka	for chromatography
Zirconium Oxide	Riedel-deHaen	pure
Zinc Oxide	Fluka	≥ 99.0% (p.a.)
Sulfuric Acid	Labscan	96 % (AR)
Stannous Chloride	Fluka	≥ 98 % (purum)
Acidic γ -Alumina	Alfa Aesar	96% Assay
Beta Zeolite	Zeolyst Int'l	$\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$
NaX Zeolite	Aldrich	Molecular sieves Ave. Part.~2 μ
NaY Zeolite	UOP	Molecular Sieve Type Y-54

At 65-70°C, the equipment used is shown in Figure 3.2. The reaction was done in a 100-ml three necked flask equipped with a reflux condenser, sampling port and thermocouple. The flask was placed in a furnace with PID controller and temperature transducer. The magnetic stirrer was used to provide agitation. While at temperatures higher than 70°C and pressure above 1 atm, the reactor used is shown in Figure 3.3 that is a Parr series (300 ml) pressurized reactor with a programmable PID controller.

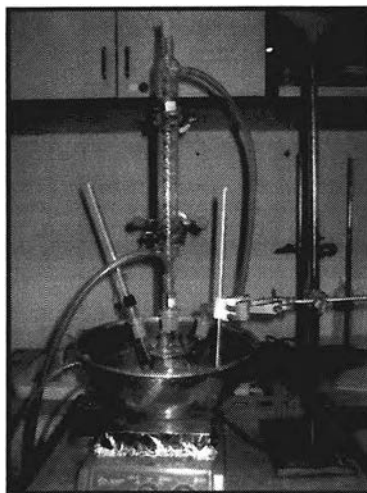


Figure 3.1 Experimental set-up used for the study of homogeneous catalyst.

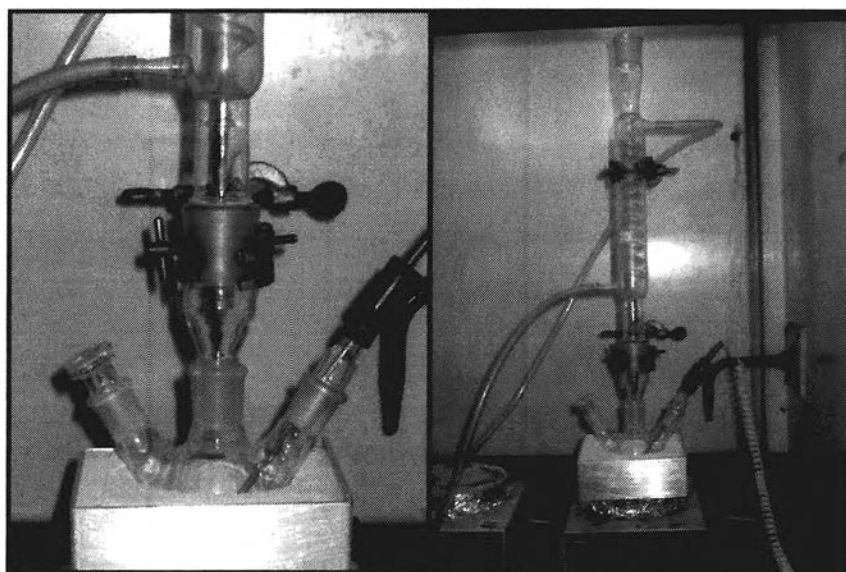


Figure 3.2 Experimental set-up used for the study of heterogeneous catalyst at 65-70°C.

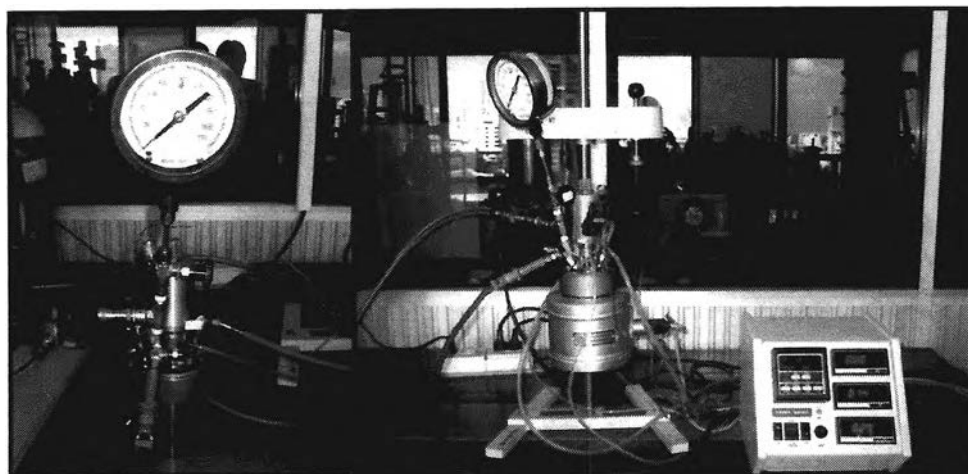


Figure 3.3 Parr reactor set-up.

3.3 Methodology

3.3.1 Characterization of Vegetable Oils

The crude PKO and CCO were analyzed based on density at 27°C, kinematic viscosity (ASTM D-445), free fatty acid content (AOCS Cd 3a-63), moisture content (AOCS Aa 3-38) and fatty acid composition (AOCS Ce 1-62).

3.3.2 Transesterification of Vegetable Oils Using Homogeneous Catalysts

One hundred grams of oil was weighed and placed in a 3-neck round bottom flask. The oil was heated to 60°C. The desired amount of NaOH and methanol were weighed and mixed until all the catalyst was dissolved and then heated to 60°C. The methoxide solution was added to the flask. The temperature was raised to 65°C and stirred for an hour. The flask was then immersed in a room temperature water bath to stop the reaction. The mixture was placed in a separatory funnel and was allowed to stand overnight to insure the separation of the methyl ester and the glycerol phase. The glycerol phase was removed and placed in a separate container. Afterwards the methyl ester layer (top layer) was washed with warm distilled water (50°C) until the water layer was clear to insure the removal of soap.

Then the excess methanol was removed by rotary evaporation at 50°C under vacuum. Finally, the methyl esters was dried by adding sodium sulfate (20% based on the weight of washed methyl ester).

The parameters affecting the reaction were studied by fixing the reaction temperature to 65°C and reaction time to 1 hr. The conditions used are shown in Tables 2.1 and 2.2.

Samples PKO 1-3 and CCO 1-3 were done to determine the effect of the amount of NaOH catalyst. While samples PKO 3-7 and CCO 3-7 were done to determine the effect of methanol: oil ratio in the transesterification. The effect of water in the reaction was studied using PKO 8-9 and CCO 8-9.

3.3.3 Transesterification of Vegetable Oils Using Heterogeneous Catalysts

The crude coconut oil was used in the screening of possible heterogeneous catalysts. All catalysts were calcined at 400°C for 5 hr. The conditions used are listed in Table 3.4.

Only the Sulphated-SnO₂ was prepared using the method outlined by Chavan *et al.* (1996). 22.56 g of stannous chloride was dissolved in 200-ml distilled water to get a clear solution. 25 ml of aqueous ammonium hydroxide was added to this solution with stirring until pH 8. The yellowish precipitate thus obtained was washed well with distilled water, dried at 110°C for 12 hours to get stannous hydroxide. 5 g of the dry hydroxide powder was then equilibrated with 25 ml of 2 N H₂SO₄ for 2 hr. Then it was evaporated to dryness and calcined at 500°C for 4 hr.

Table 3.2 Conditions used for crude palm kernel oil

Experiment No.	Amount of NaOH as catalyst (% based on weight of oil)	Methanol: Oil Molar Ratio
1	0.1	10:1
2	0.5	10:1
3	1.0	10:1
4	1.0	20:1
5	1.0	6:1
6	1.0	4:1
7	1.0	3:1
8	0.5	6:1
9	0.5	6:1 (dried oil)

Table 3.3 Conditions used for crude coconut oil

Experiment No.	Amount of NaOH as catalyst (% based on weight of oil)	Methanol: Oil Molar Ratio
1	0.1	10:1
2	0.5	10:1
3	1.0	10:1
4	1.0	20:1
5	1.0	6:1
6	1.0	4:1
7	1.0	3:1
8	0.5	6:1
9	0.5	6:1 (dried oil)

Table 3.4 Conditions used in the investigation of possible heterogeneous catalyst

Experiment No.	Catalyst	Amt. Cat. %	MeOH: Oil ratio	Temperature °C	Reaction Time, hr
1	Na ₂ CO ₃	6	20:1	65-70	10
2	K ₂ CO ₃	6	20:1	65-70	10
3	CaCO ₃	6	20:1	65-70	10
4	ZrO ₂	6	20:1	65-70	10
5	ZnO	6	20:1	65-70	10
6	Beta	6	20:1	65-70	10
7	NaX	6	20:1	65-70	10
8	NaY	6	20:1	65-70	10
9	Al ₂ O ₃	6	20:1	65-70	10
10	S·SnO ₂	6	20:1	65-70	10
11	K ₂ CO ₃	6	20:1	30	6
12	----	---	10:1	200 ^{50 bar}	4
13	K ₂ CO ₃	6	10:1	200 ^{50 bar}	4
14	CaCO ₃	6	10:1	200 ^{50 bar}	4
15	ZrO ₂	6	10:1	200 ^{50 bar}	4
16	ZnO	6	10:1	200 ^{50 bar}	4
17	Beta	6	10:1	200 ^{50 bar}	4
18	NaX	6	10:1	200 ^{50 bar}	4
19	NaY	6	10:1	200 ^{50 bar}	4
20	Al ₂ O ₃	6	10:1	200 ^{50 bar}	4
21	S·SnO ₂	6	10:1	200 ^{50 bar}	4

3.3.4 Analysis of Methyl Esters

The methyl ester samples were analyzed by high-performance liquid chromatography (HPLC) at Thailand Institute of Scientific and Technological Research Center using a Shimadzu Series LC-pump and a refractive index Series detector and controlled by a PC with a software package (Shimadzu Chromatopac). A Spherisorb ODS-II C18 column (4.6 mm x 250 mm x 5 μ m) was used and the mobile phase was an acetone/acetonitrile mixture (50:50 vol/ vol) at a flowrate of 0.7 ml/min. The column temperature used was at 40°C. The pump pressure was operated in the range of 25-32 psi. Samples were diluted with acetone (2.5 g sample in 5 ml mixture) and the injection volume was 20 μ l.